

SUPPLEMENTARY MATERIAL

**Quantification of Twenty-one Metabolites of Methylnaphthalenes and Polycyclic Aromatic
Hydrocarbons in Human Urine**

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Accurate mass peak profiling for peak confirmation

Identity of the Me-OHN peaks in urine samples was confirmed by the use of mass peak profiling (Grant et al., 1994) at mass resolution of 10,000 on a magnetic sector high-resolution mass spectrometer (MAT95XL, Thermo Fisher Scientific Inc. Waltham, MA, USA). The calculated exact mass for the molecular ion and 16 additional masses, 8 on each side of the exact mass at an increment of 10 ppm, were monitored as the capillary GC peaks eluted. Mass profiles were constructed by plotting ion abundance as a function of mass. The apex of the mass profiles in a urine sample matched the exact mass and that from a standard, confirming the identity of the Me-OHN peaks.

Reference:

Grange AH, Donnelly JR, Brumley WC, Billets S, Sovocool GW. (1994) Anal Chem. 66:4416-4421

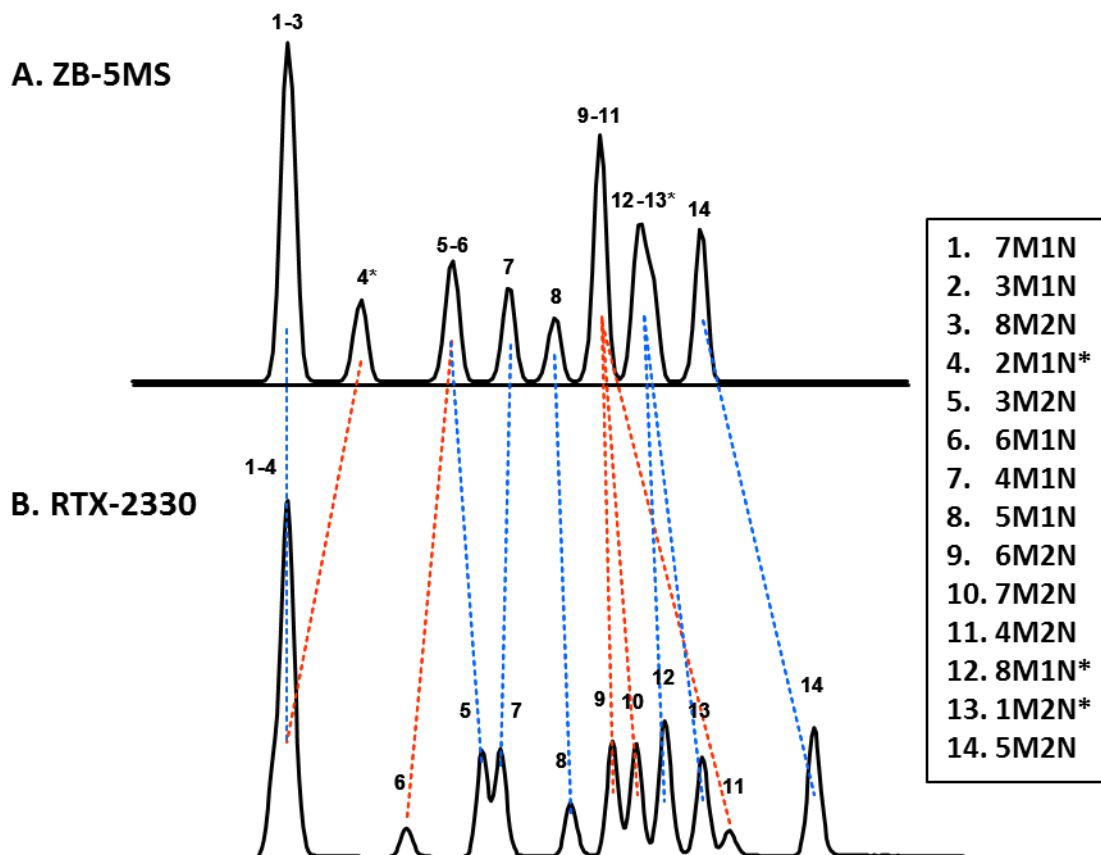
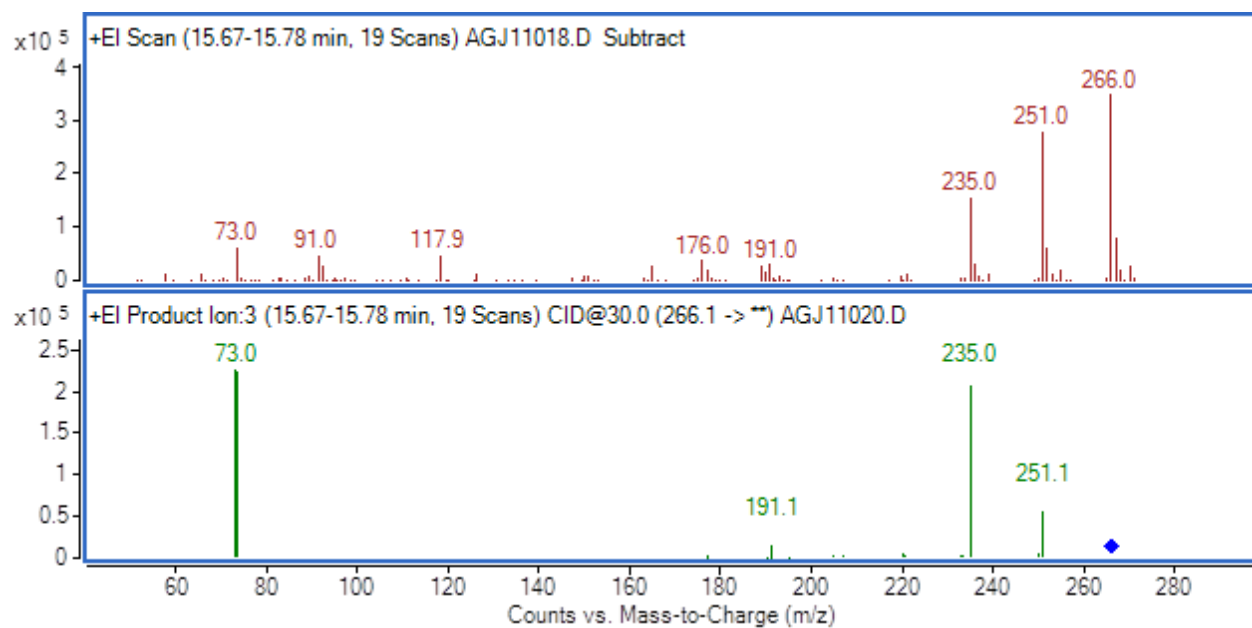


Figure S1. GC chromatograms of 14 methyl naphthols on (A) a non-polar ZB-5MS column and (B) a polar Rtx-2330 column. Peaks represent the trimethylsilyl ethers of OH-PAHs and Me-OHNS. Peaks marked with an asterisk are isomers that are not reported in this method.



1
2 Figure S2. A full scan spectrum of the trimethylsilyl ether of 1-hydroxyphenanthrene (top) and a
3 product ion scan of its molecular ion (bottom).

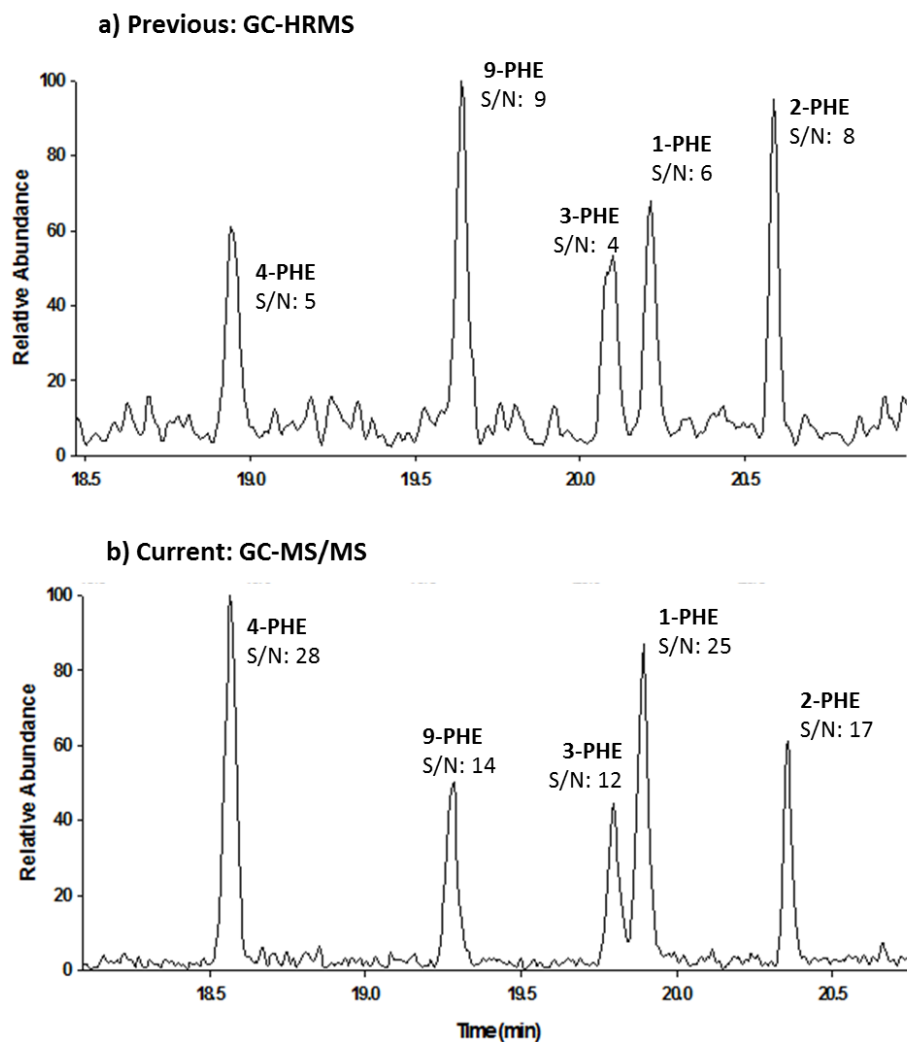


Figure S3. GC chromatograms of the lowest calibration standard (25 fg on column) from the previous method using GC high resolution mass spectrometry (GC-HRMS) (a) and the current method using GC-MS/MS (b). Peaks represent the trimethylsilyl ethers of OH-PAHs and Me-OHNs.

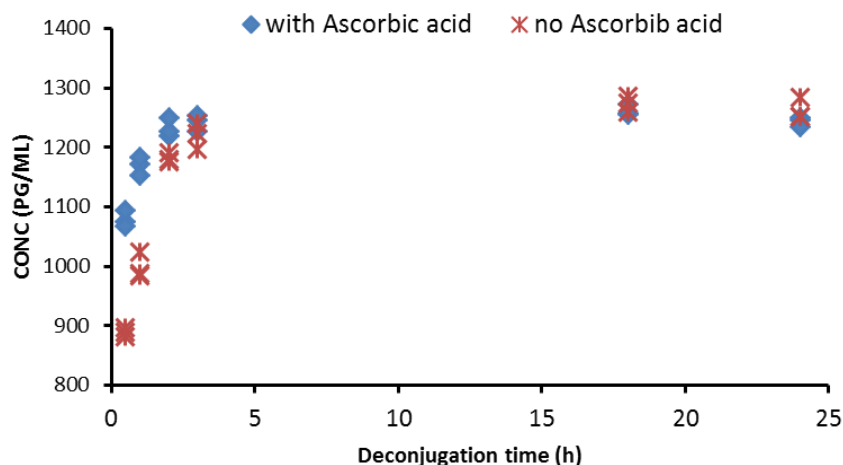


Figure S4. Calculated concentrations of 9-hydroxyfluorene in a smoker's urine sample as a function of deconjugation time (1, 2, 3, 18 and 24 h), with or without ascorbic acid (2.5 mg/mL urine) during hydrolysis.

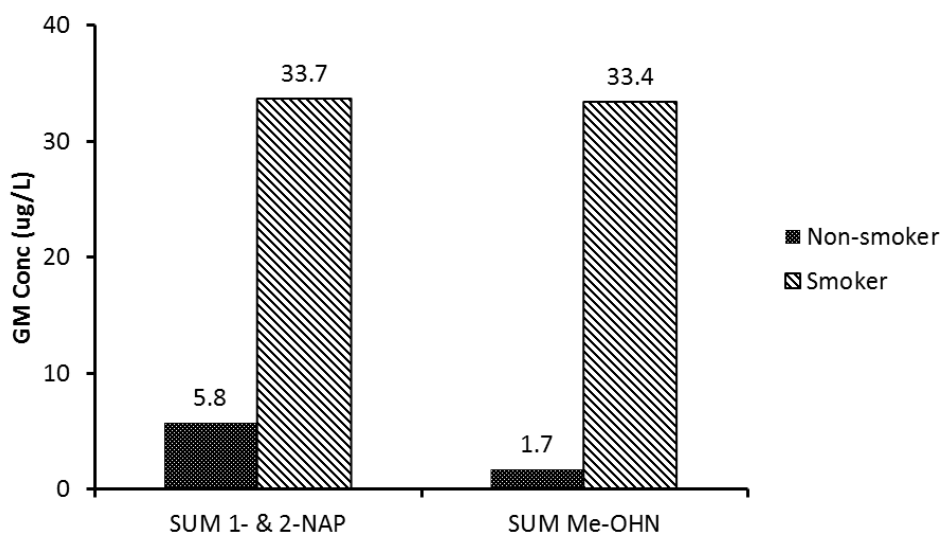


Figure S5: Geometric mean concentrations of summed 1- and 2-naphthols (metabolites of naphthalene) and summed methyl naphthols (metabolites of 1- and 2-methylnaphthalene) in 30 smokers and 30 non-smokers.